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Mechanical properties of weakly segregated block copolymers
2. The influence of phase behaviour on tensile properties of poly(styrene-b-butylmethacrylate) diblock copolymers

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Abstract

The tensile properties of poly(styrene-b-butylmethacrylate) diblock copolymers (PS-b-PBMA) were investigated depending on volume fraction of polystyrene (with a constant molecular weight of $\bar{M}_n \approx 100$ kg/mol) and overall molecular weight (constant volume fraction of 65–70% PS). Diblock copolymers in the composition range 37–57% PS show lamellar structures and a partial miscibility due to their weakly segregated phases. In contrast, samples with other compositions are disordered. A transition from ductile to brittle properties was observed at a PS-content of 57%. Using different molecular weights, it was possible to correlate the different states of segregation (disordered, weak and intermediate segregation) with tensile properties where a change from brittle to ductile properties can be found with increasing molecular weight due to the transition from disordered to an ordered state. At higher molecular weights the phases are intermediately segregated and a maximum in tensile strength as well as strain-at-break can be observed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(styrene-b-butylmethacrylate) diblock copolymer; Mechanical properties; Phase behaviour

1. Introduction

Block copolymers provide the possibility to create new materials with improved mechanical properties because of their tendency to microphase separation on the nanometre scale resulting in differently ordered morphologies. Thermoplastic elastomers (TPE) are one example of a technical application of block copolymers. Another example is the interfacial modification of polymer blends, where block copolymers can enhance the interfacial adhesion between immiscible components [1].

Poly(styrene-b-isoprene) (PS-b-PI) diblock copolymers were the subject of many investigations during the last years [2], which have shown that the following classical morphologies exist: BCC-spheres, hexagonal packed cylinders, ordered bicontinuous double diamond (OBDD) and lamellar structures [3–6]. Recently, near the order–disorder transition perforated layers and the cubic bicontinuous structure (“gyroid”) was found. Order–order transitions between these morphologies also exist depending on block length and interaction parameter (χN) [7–9]. Recently, Stadler et al. [10–12] reported new morphologies in block copolymers consisting of three different components.

Russell et al. [13,14] have found a microphase separation of poly(styrene-b-butylmethacrylate) (PS-b-PBMA) diblock copolymer melts on heating. SAXS experiments have shown the existence of both an upper critical order transition (UCOT) and a lower critical order transition (LCOT) [13]. Furthermore, Ruzette et al. [15] have shown that dPS-b-alkylmethacrylate diblock copolymers with long alkyl side chains ($n \geq 6$) reveal an UCOT behaviour. In contrast, diblock copolymers with short side chain methacrylates ($n < 5$) reveal an LCOT behavior.

In our previous papers, we reported the morphology, phase behaviour, interface formation, and tensile properties of PS-b-PBMA diblock copolymers with molecular weights of $M_n > 200$ kg/mol [16–20]. It was shown that PS-b-PBMA diblock copolymers show improved tensile properties [16,17]. In contrast to other polymeric systems we have found that the tensile strength for PS-b-PBMA diblock copolymers in the composition range 70–80% PS significantly exceeds the value of PS. In this study the influence of the phase behaviour on mechanical properties of PS-b-PBMA diblock copolymers will be presented.

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Table 1
Molecular weight (M_n), volume fraction (Φ_{PS}) and polydispersity (M_w/M_n), χN values at 120°C (determined from Eq. (1)) and morphology (TEM) for PS-b-PBMA diblock copolymers used in this study

Sample	$10^{-3} \times M_n$[a] copolymer	M_w/M_n	Φ_{PS}-Block[b]	Morphology (TEM)	χN
Series 1					
P17	100.8	1.02	0.17	Disordered	9.5
P27	75.9	1.08	0.27	Disordered	7.4
P37	123.0	1.10	0.37	Lamellae	12.5
47	123.0	1.05	0.47	Lamellae	12.9
P57	98.4	1.03	0.57	Lamellae	10.6
P67	94.0	1.05	0.67	Disordered	10.4
P77	110.8	1.02	0.77	Disordered	12.6
P90	100.1	1.04	0.9	Disordered	11.8
Series 2					
SBM72	71.8	1.06	0.68	Disordered	8.0
SBM94	94.0	1.05	0.67	Disordered	10.4
SBM130	130.0	1.06	0.70	Lamellae	14.6
SBM270	270.0	1.06	0.70	Lamellae	30.3
SBM315	315.0	1.08	0.70	Lamellae	35.4
SBM450	450.0	1.05	0.67	Lamellae	50.1

[a] Total molecular weight and polydispersity determined by size exclusion chromatography (SEC), values are based on the PS standards.
[b] Volume fraction of PS determined by ^{1}H NMR.

2. Experimental details

2.1. Polymerization: general procedure

All polymerizations were carried out in carefully flamed glass reactors in THF as the solvent at −78°C under an argon atmosphere using syringe techniques. After several cycles of degassing from calcium hydride, styrene was introduced into the reactors by condensation under reduced pressure. THF was condensed from oligomeric polystyrene anions. Then the desired amount of initiator was added at once and after 15 min the living polystyrene anions were end-capped with diphenylethylene. Butyl methacrylate as the second monomer was added dropwise very slowly by syringe. The activity of the living anions was terminated by adding methanol after another 30 min. Then the polymer was precipitated in a 7/3 methanol/water mixture at −30°C, washed and dried in vacuo for several days. Size exclusion chromatography (SEC) measurements were carried out using a Knauer-SEC with a RI/Viscodetector and a PSS linear column.

2.2. Sample preparation

All samples were cast from toluene, and the solvent was allowed to evaporate slowly over 5–7 days at room temperature. The films were then dried to constant weight in a vacuum oven at 120°C for 3 days.

2.3. Investigations

The dynamic elastic and loss shear moduli, G' and G'', were determined with a Rheometrics RDAII rheometer using the temperature step mode and a frequency of 1 Hz. Samples for dynamic mechanical measurements (DMA) had a thickness of 1 mm. The glass transition temperature (T_g) is defined as the maximum in G''.

Ultrathin sections (50 nm) were cut at room temperature using glass knives in a Ultramicrotome (Reichert). The polystrene block were stained with RuO_4 vapour. Transmission electron microscopic (TEM) investigations were performed by using the microscope BS 500.

Tensile tests were performed using a universal testing machine (Zwick 1425) at a strain rate of $1.6 \times 10^{-4}\ s^{-1}$. This small strain rate was used in order to prevent a premature failure of the samples so that the change of tensile properties can be correlated to the phase behaviour. The tensile specimens had a thickness of 0.5 mm and a total length of 50 mm. The toughness of the diblock copolymers was estimated as absorbed energy from the stress–strain curves. For each stress–strain curve at least 10 samples were measured. For analysis of data only those samples where the failure occurred within the gauge length were used. All investigated samples were prepared by solvents which have a pronounced influence on tensile properties. Fracture surfaces were investigated qualitatively from tensile test specimens using a scanning electron microscope (SEM, Jeol).

3. Results and discussion

3.1. Phase behaviour

Two series of PS-b-PBMA diblock copolymers were synthesized with (1) an overall molecular weight of $\bar{M}_n = 100$ kg/mol and different polystyrene contents and (2) different molecular weights with an approximately constant polystyrene content of about 65–70%. The

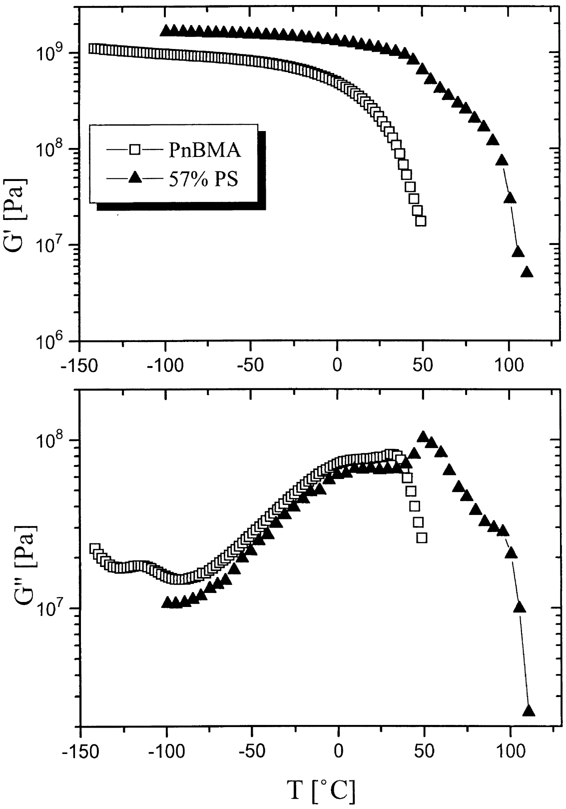

Fig. 1. Dependence of storage modulus (G') and loss modulus (G'') on the temperature for P57 ($\Phi_{PS} = 0.57$, $M_n = 98$ kg/mol) and pure PBMA measured at a frequency of 1 Hz.

molecular weights, polystyrene contents and morphologies of the diblock copolymers used in this study are summarized in Table 1.

As already described in our previous paper [18] PS-b-PBMA diblock copolymers reveal a partial miscibility in the high molecular weight range, $M_n > 200$ kg/mol. Partial miscibility is also observed for diblock copolymers with molecular weights of $\bar{M}_n = 100$ kg/mol and PS contents of 37–57%. For diblock copolymers in this composition range two glass transition temperatures (T_g) are observed. While the T_g of the PBMA-block is shifted to higher temperatures, that of the of the PS block is not affected and remains constant at 100°C (Fig. 1). This confirms our assumption of partial miscibilty of these samples, because for weakly segregated block copolymers mixed phases exist due to the broadened interface between the components. As shown in Fig. 1, near the glass transition of the PBMA rich phase a β-relaxation exists due to the rotation of the butyl ester side group as already observed by Heijboer for PBMA [21].

An approximately linear dependence of T_g of the PBMA-block on PS-content exists in the composition range of $0.37 < \Phi_{PS} < 0.57$ (Fig. 2). The T_g of the PBMA-block for sample P47 (123 kg/mol, 47% PS) is shifted by up to 47°C and for sample P57 (98.4 kg/mol, 57% PS) by up to 50°C. For both samples, the T_g of the PS block remained at 100°C. This means that an essentially pure PS phase existed together with a PS/PBMA mixed phase. To explain this phenomenon we have to assume an asymmetrical phase diagram for PS-b-PBMA diblock copolymers [20,22]. For diblock copolymers with PS-contents of $\Phi_{PS} < 0.37$ and $\Phi_{PS} > 0.57$ only one broadened glass transition is obtained (Fig. 3) which means that these samples are disordered.

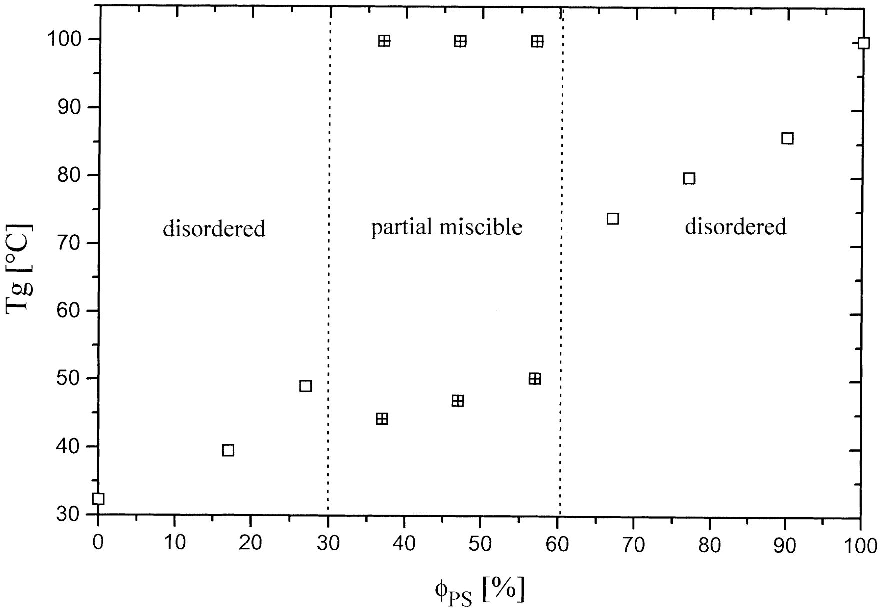

Fig. 2. Dependence of the glass transition temperature on the volume fraction Φ_{PS} for $M_n \approx 100$ kg/mol.

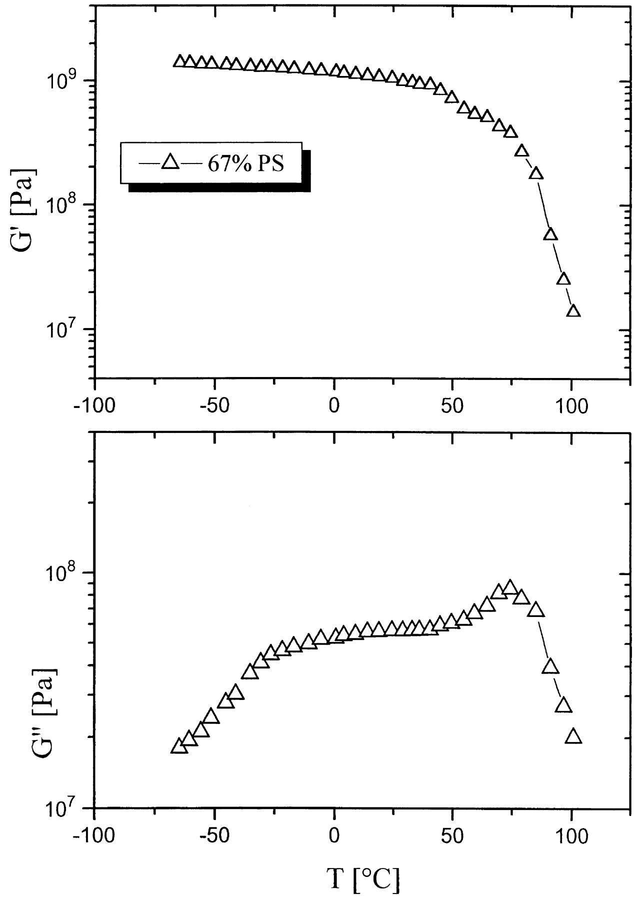

Fig. 3. Dependence of storage modulus (G') and loss modulus (G'') on the temperature for P67 ($\Phi_{PS} = 0.67$, $M_n = 94$ kg/mol) measured at a frequency of 1 Hz.

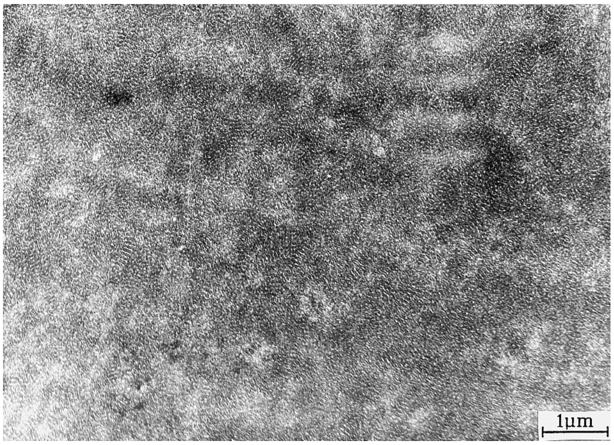

Fig. 4. TEM micrograph of sample SBM130 with lamellar structure ($\Phi_{PS} = 0.70$, $M_n = 130$ kg/mol) where the microphases are weakly segregated.

Near the order–disorder transition the fluctuations in composition will be relevant due to the increase of the interaction parameter χ. As a result the chains build up A-rich and B-rich phases where the concentration of A-chains in the A-rich phase and the concentration of B-chains in the B-rich phase depends on the value of χ [23]. This so-called fluctuation structure is due to fluctuation of the local concentrations which was described by Helfand and Fredrickson [24] as a correction of the mean field theory of Leibler [25]. In the case of PS-b-PBMA diblock copolymers with asymmetric compositions the broadened glass transition could be due to the fluctuation effects near the phase transition, because the UCOT and LCOT, observed by Russell and co-workers [26], are not far from the annealing temperature of the samples at 120°C. Recently, for a poly(dPS-b-nBMA) diblock copolymer with 55% PS and $M_n = 90$ kg/mol the disorder–order transition was found at 155°C by SANS and rheology [19]. From fits to the SANS profiles in the disordered state the temperature dependence of χ was determined as [19]:

$$\chi = (0.0243 \pm 0.0004) - \frac{(4.56 \pm 0.169)}{T} \qquad (1)$$

This shows clearly that for PS-b-PBMA diblock copolymers a LCOT behaviour exists for temperatures higher than 110°C. Lower temperatures are limited by the T_g of the PS block and the properties become irreversible. Russell et al. [26] have found the order–disorder transition (ODT) at approximately 80°C. However, this temperature is below the T_g of the PS block which makes it difficult to achieve the equilibrium.

Table 1 gives the χN values for all samples used in this study. It is shown that for a sample with $M_n = 123$ kg/mol and 47% PS (P47 in Table 1) χN at 120°C is 12.8. The criterion for the ODT of block copolymers was given in the theory of Leibler [25] as $\chi N = 10.5$. With increasing χN the block copolymer builds up a structure where the phases are only weakly segregated ($10.5 < \chi N < 12.5$). Within the weak segregation limit (WSL) the microscopic density profile of the components is considered to vary sinusoidally in space and the chains of the components are highly interpenetrating. The small χN values in Table 1 indicate that samples with approximately symmetrical compositions (47%, 57% PS) are weakly segregated. This confirms the partial miscibility of these block copolymers found by DMA. In this case, microphase separated morphologies can be expected for nearly symmetrical diblock copolymers, which was confirmed by TEM [18]. For block copolymers in the WSL a broadened interface can be expected. It was shown in one of our previous papers that a symmetrical poly(dS-b-*n*BMA) diblock copolymer with $M_n = 148$ kg/mol possesses an interface width of 9 nm observed by neutron reflectometry which is quite large in comparison to that of PS-b-PI diblock copolymers [19]. For asymmetric compositions $\Phi_{PS} < 0.37$ and $\Phi_{PS} > 0.57$ the χN values are in order of 7.5–12.5 at 120°C which leads to the conclusion that these samples are disordered because $(\chi N)_{crit}$ is larger than 10.5 for asymmetric block copolymers. This is confirmed by DMA where, for these samples, only one broadened glass transition was found.

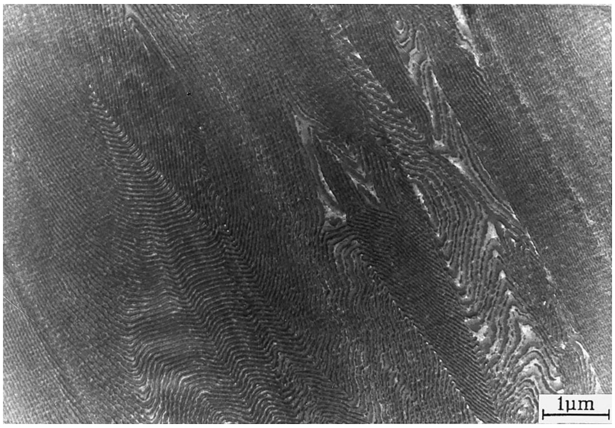

Fig. 5. TEM micrograph of sample SBM270 with lamellar structures ($\Phi_{PS} = 0.70$, $M_n = 270$ kg/mol) where the microphases are intermediately segregated.

In our previous paper [18,20] we have shown that in the case of PS-b-PBMA diblock copolymers with $M_n > 200$ kg/mol spherical, hexagonal, lamellar, perforated lamellar, and bicontinuous structures exist depending on volume fraction of PS. In this study, diblock copolymers with different molecular weights at PS contents of 65–70% are also investigated. It is observed that samples with molecular weights $M_n < 130$ kg/mol are disordered at 120°C. In contrast, samples with $M_n > 130$ kg/mol show lamellar structures. However, the morphology shown in Fig. 4 is rather disordered and shows only a small long-range order. Eq. (1) gives a χN of 14.6 for this sample, which means that this block copolymer is almost weakly segregated. In contrast, for a sample with $M_n = 270$ kg/mol and 70% PS (SBM70) χN is about 30 which leads to the conclusion that this sample is intermediately segregated. It is shown in Fig. 5 that the lamellar structure of this sample is highly ordered arising from the stronger incompatibility with increasing molecular weight. This means that block copolymers with molecular weights $M_n < 100$ kg/mol are disordered and samples with about 130 kg/mol are weakly segregated. With increasing molecular weight the increase of χN is combined with an intermediate segregation of the phases. It has already been discussed elsewhere [19,20] that samples with molecular weights of 200–400 kg/mol are intermediately segregated which was confirmed by the measured large interface width. As discussed above, for asymmetric compositions, $(\chi N)_{crit}$ increases which leads to the assumption that a block copolymer with $M_n = 130$ kg/mol containing 70% PS (sample SBM130) is weakly segregated at 120°C. This results in a lamellar structure with small long-range order as shown in Fig. 4 (sample SBM130, 130 kg/mol, 70% PS).

It should be mentioned that we compared deuterated (SANS [19]) and non-deuterated samples (samples investigated in this paper) and we found that deuteration could also change the thermodynamics of the block copolymers. Furthermore, a possible dependence of χ on composition was also neglected in our discussion.

3.2. Mechanical properties

For PS-b-PBMA diblock copolymers with $\Phi_{PS} < 0.67$ a strong increase in tensile strength with increasing PS content is observed (Fig. 6). The same result was found for diblock copolymers for molecular weights $\bar{M}_n > 200$ kg/mol [16]. In contrast, for the block copolymers with molecular weights $\bar{M}_n \approx 100$ kg/mol used in

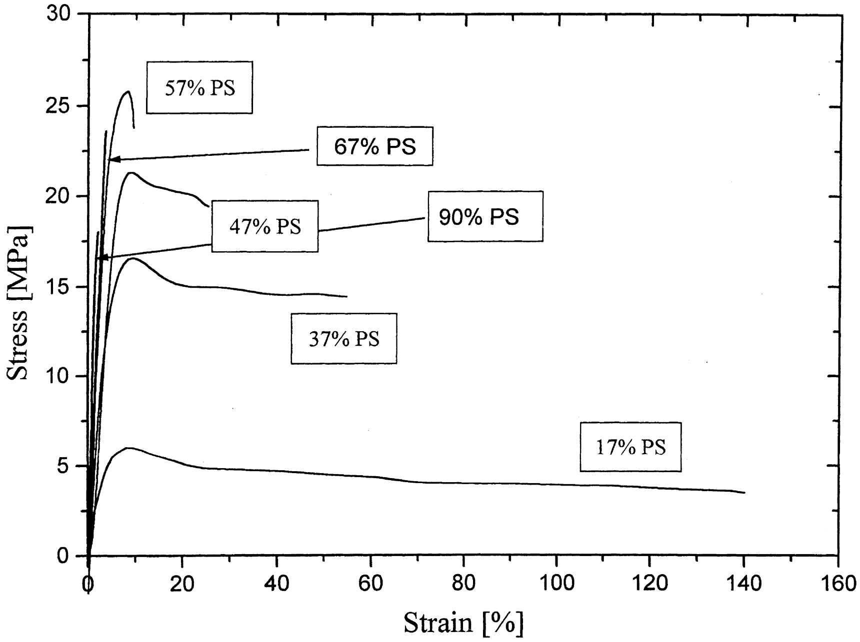

Fig. 6. Stress–strain curves for diblock copolymers with $M_n \approx 100$ kg/mol at a strain rate of $\dot{\varepsilon} = 1.6 \times 10^{-4}$ s^{-1} (sample series 1 in Table 1).

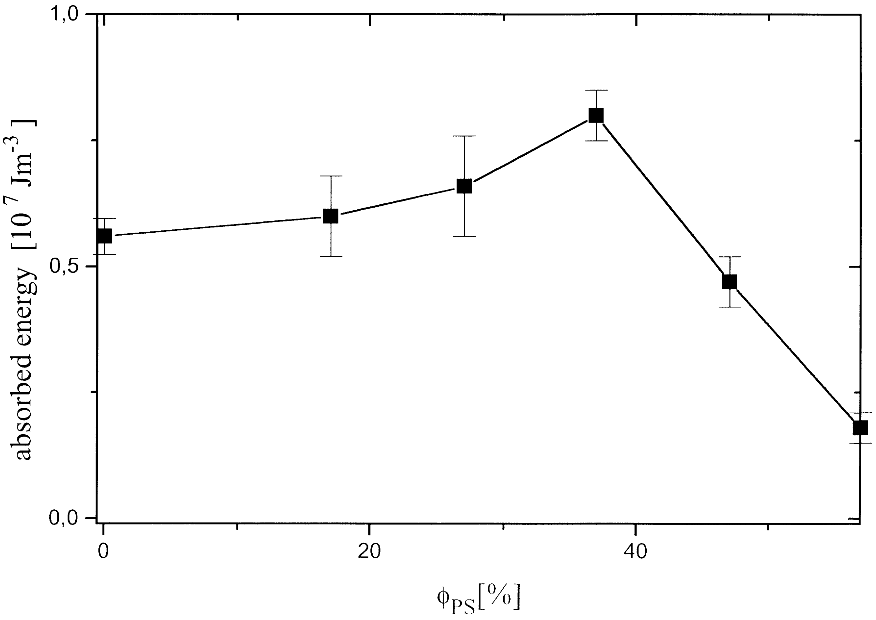

Fig. 7. Dependence of the absorbed energy on the volume fraction Φ_{PS} at a strain rate of $\dot{\varepsilon} = 1.6 \times 10^{-4}\ s^{-1}$.

this study, the tensile strength does not exceed the value for PS. As shown in Fig. 6, the maximum of tensile strength can be observed for a sample with 57% PS which displays a lamellar structure. The tensile strength at this composition is almost the same as that for PS, which is a surprising result if one takes into account that the PS content of this sample is only 57%. The result that the tensile strength of PS-b-PBMA diblock copolymers is generally higher than those observed for PS-b-PB diblock copolymers can be attributed to the thermoplastic properties of both components, PS and PBMA.

The tensile stength shows a steeper increase in the composition range $0.37 < \Phi_{PS} < 0.57$ than observed for diblock copolymers with small PS contents (Fig. 6). Our previous investigations [18] have shown that in this composition range lamellar structures exist. In contrast, diblock copolymers with a polystyrene content of $\Phi_{PS} > 0.57$ become brittle and show almost the same behaviour of PS with a molecular weight of 100 kg/mol.

In the composition range $0.37 < \Phi_{PS} < 0.57$, where the tensile strength strongly increases, a partial miscibility was observed. For these samples the tensile strength shows a steeper increase than expected from a linear dependence on polystyrene content. For diblock copolymers with PS contents $\Phi_{PS} > 0.57$ the observed brittle properties can be attributed to the disordered morphological state of these samples. Also the small χN values indicate the disordered state at these compositions. This indicates that the transition from ductile to brittle behaviour at 67% PS could be attributed to the transition to the disordered state at this composition. This will be discussed later using samples with different molecular weights. The tensile properties of brittle materials often show larger error bars due to voids and other inhomogeneities arising from preparation effects. Stress concentrations at inhomogeneities act to localize the deformation, often causing premature failure. All samples used in this study, were prepared from solvents which have a strong influence on mechanical properties. Therefore, the discussed properties cannot directly be compared with commercially manufactured materials.

The absorbed energy, estimated from the tensile stress–strain curves, shows a maximum at a PS content of $\Phi_{PS} = 0.37$ due to a lamellar morphology at this PS content (Fig. 7). A further increase in PS content up to 57%, leads to a decrease in absorbed energy. This means that a higher amount of PBMA, which is connected with an increasing thickness of the PBMA-lamellae, is necessary for an enhancement of the energy absorbed. The dependence of absorbed energy on the volume fraction of PS for compositions with higher than 57% PS is not discussed, because these samples exhibit brittle properties. As already mentioned, the tensile properties of polymers with brittle behaviour are strongly influenced by the method of preparation. For PS-b-PBMA diblock copolymers with higher molecular weights of $M_n > 200$ kg/mol, a maximum in the absorbed energy was observed at $\Phi_{PS} = 0.35$ which is in agreement with the result observed for samples with $M_n \approx 100$ kg/mol investigated in this study. For block copolymers with $M_n > 200$ kg/mol hexagonally packed PS cylinders were observed at 35% PS and the absorbed energy is larger than that observed for diblock copolymers with $M_n \approx 100$ kg/mol [16]. This leads to the conclusion that a morphology of hexagonally packed PS cylinder seems to be very effective for an enhancement of absorbed energy.

In order to investigate the influence of molecular weight

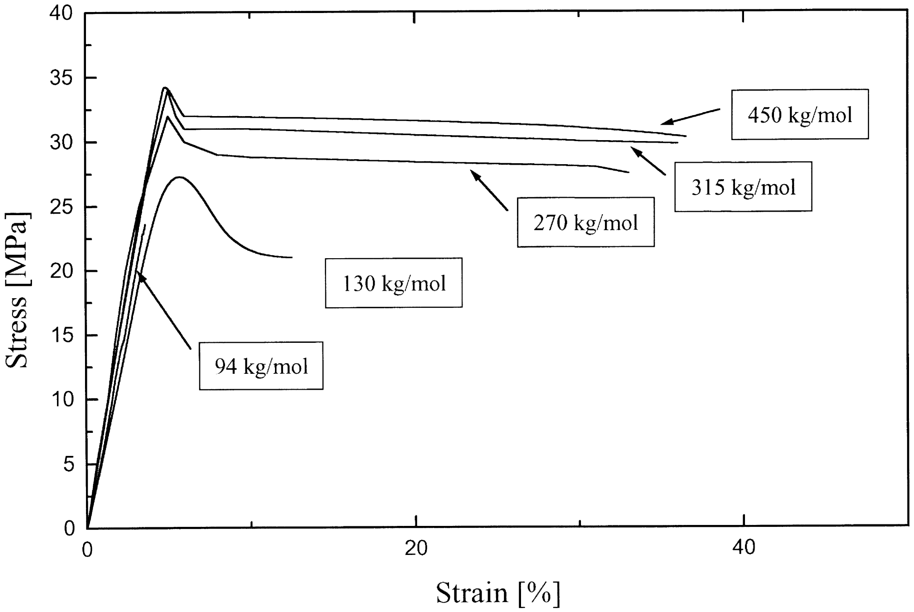

Fig. 8. Stress–strain curves for diblock copolymers depending on molecular weight at a PS content of approximately 70% at a strain rate of $\dot{\varepsilon} = 1.6 \times 10^{-4}\ \mathrm{s}^{-1}$ (series 2 in Table 1).

on mechanical properties a second series of samples with different molecular weights (72–450 kg/mol) and an approximately constant amount of PS (65–70% PS) was used (series 2 in Table 1: samples SBM72–SBM450). In Fig. 8 the stress–strain curves for these samples are shown. It is obvious that samples with molecular weights $M_n < 130$ kg/mol are brittle. In contrast, block copolymers with molecular weights $M_n \geq 130$ kg/mol are ductile indicated by the yield point at lower strains. This leads to the conclusion that for samples with 130 kg/mol a change of fracture mode from brittle to ductile occurs. This causes higher strains-at-break for samples with high molecular weights of 270–450 kg/mol. As shown in Figs. 9 and 10, the fracture surfaces are markedly different for block copolymers with 94 kg/mol (SBM94 in Table 1) as compared to that of sample SBM270 with 270 kg/mol. For sample SBM270, it is seen in Fig. 10 that a large degree of plastic deformation occurs during fracture which is not observed in Fig. 9 for sample SBM94. While the plane and nearly non-deformed fracture surface at 94 kg/mol (Fig. 9) can be related to their brittle property, for block copolymers with 270 kg/mol (Fig. 10) the plastic deformation is related to a macroscopic stress whitening observed during tensile tests. This indicates a change of fracture mode with increasing molecular weight already shown in the stress–strain curves in Fig. 8. Furthermore, a transition from crazing to cavitation mechanism can be observed with increasing molecular weight, which, however, will be discussed elsewhere [27].

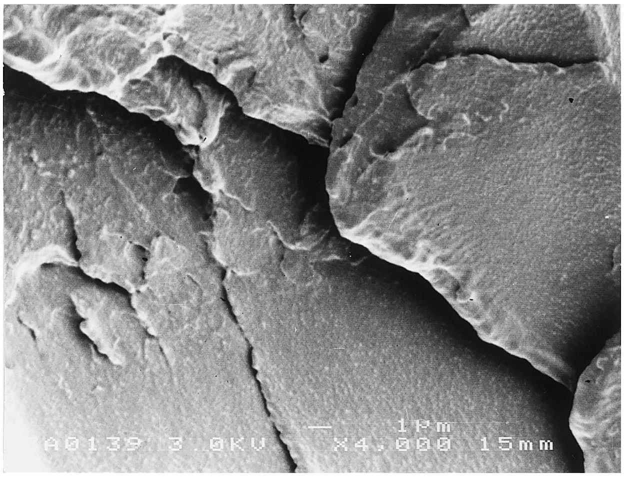

Fig. 9. SEM micrograph of fracture surface of sample SBM94 (94 kg/mol; 67% PS).

In Figs. 11 and 12 the dependence of tensile strength and strain-at-break on the overall molecular weight of the diblock copolymers are shown. For molecular weights $M_n < 130$ kg/mol a strong decrease in tensile strength as well as strain-at-break is observed. A maximum of tensile strength and strain-at-break exists for molecular weights $M_n > 315$ kg/mol. For molecular weights $M_n < 100$ kg/mol the small strength and strain-at-break are due to the disordered state of these block copolymers. For a diblock copolymer with a molecular weight of 130 kg/mol (70% PS, sample SBM130) a lamellar morphology was found by TEM, which leads to an improvement in tensile strength as well as of strain-at-break. This means that the transition to ordered state at 130 kg/mol is responsible for the improved tensile properties in the molecular weight regime 130–270 kg/mol indicated by the change from brittle to ductile properties (Figs. 11 and 12). It should be mentioned that for small molecular weights of about 70 kg/mol and lower the dependence of tensile properties of the PS block

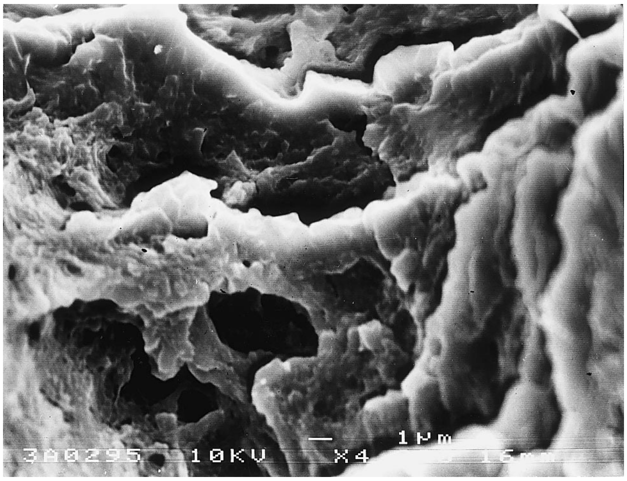

Fig. 10. SEM micrograph of fracture surface of sample SBM270 (270 kg/mol; 70% PS).

on molecular weight could also have an influence which is in accordance with the results obtained by Bühler for PS-b-PB diblock copolymers [28].

As already discussed, diblock copolymers with a molecular weight of 130 kg/mol are weakly segregated. In contrast to this, block copolymers with molecular weights of 270–450 kg/mol are intermediately segregated [20] where ordered morphologies can be found with a broadened interface width [22]. It was shown by various authors that between the weak and strong segregation limits an intermediate segregation regime (ISR) between $12.5 < \chi N < 95$ can be identified (crossover between ISR and SSL at $\chi \approx 50$ [29]), where the chains stretched due to the coarsening of the density profile as χN is increased from the WSL [30]. As shown in Figs. 11 and 12 the displayed values of χN indicate the discussed transitions from disordered state to WSL and ISR. This clearly shows that the phase behaviour has a pronounced influence on tensile properties of block copolymers. Thus block copolymers in an ordered state exhibit improved mechanical properties as compared to those in the disordered state. The large interface width observed by neutron reflectometry [19] provides an explanation for the improved tensile properties of weakly segregated block copolymers in comparison with other polymeric systems.

The high value of tensile strength at high molecular weights in the composition range of 70–80% PS, which markedly exceeds the value of pure PS [16,20] can be explained by the complex correlation between partial miscibility (weak or intermediate segregation), interface formation and deformation mechanisms of PS-b-PBMA diblock copolymers. In contrast to PS-b-PBMA diblock copolymers with $M_n > 200$ kg/mol [17,20], which show a further increase of tensile strength up to 76% PS, for diblock copolymers with $M_n \approx 100$ kg/mol, used in this study, a transition to brittle properties was observed at 67% PS. While diblock copolymers with $M_n > 200$ kg/mol show lamellar structures at 70% PS, a coexistence of lamellae and hexagonally packed PBMA-cylinder at 72–74% PS, and hexagonally packed PS cylinder at 76% PS [16,20], diblock copolymers used in this study ($\bar{M}_n \approx 100$ kg/mol) are disordered at the same compositions.

4. Conclusions

These investigations have shown that the tensile properties of PS-b-PBMA diblock copolymers are strongly influenced by phase behaviour.

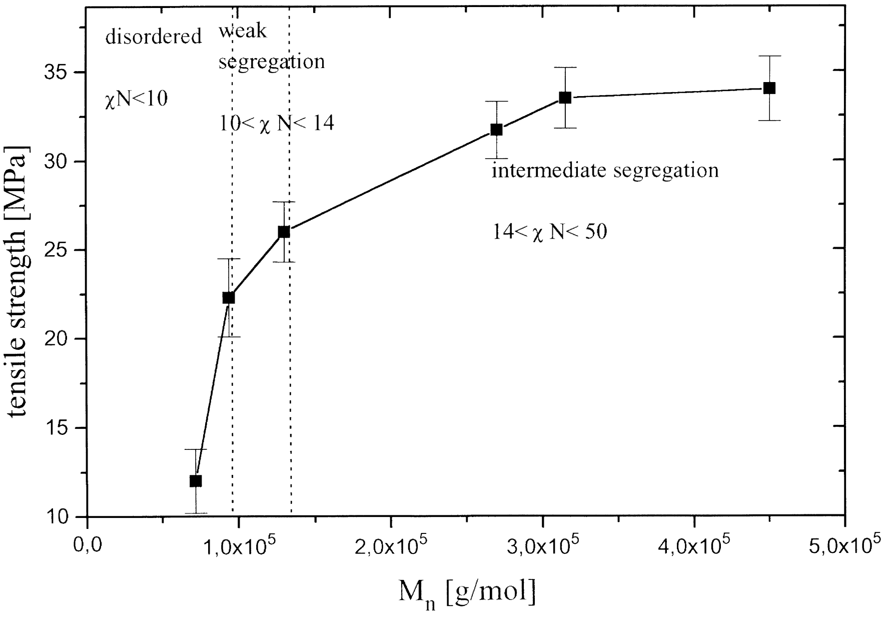

Fig. 11. Dependence of tensile strength on molecular weight for PS-b-PBMA diblock copolymers of series 2 in Table 1.

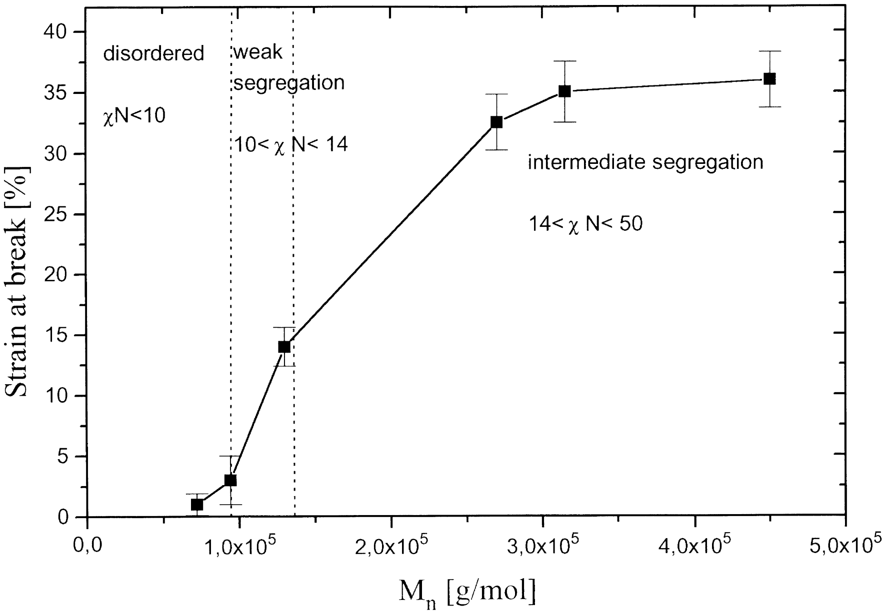

Fig. 12. Dependence of strain-at-break on molecular weight for PS-b-PBMA diblock copolymers of series 2 in Table 1.

PS-b-PBMA diblock copolymers with $M_n \approx 100$ kg/mol are disordered in the composition range of $\Phi_{PS} < 0.37$ and $\Phi_{PS} > 0.57$. In contrast, block copolymers in the composition range 37–57% PS have lamellar structures and two T_gs are observed (by TEM and DMA). These samples are weakly segregated which is in agreement with the partial miscibility found by DMA. For samples with PS contents $\Phi_{PS} > 0.57$ a change from ductile to brittle properties is observed, reflecting the change from an ordered to a disordered state.

The influence of molecular weight on mechanical properties of PS-b-PBMA diblock copolymers can be correlated to their phase behaviour and interface formation. It is shown that the state of segregation (disordered, weak or intermediate) has a pronounced influence on tensile properties of block copolymers. The change from brittle to ductile properties, observed at a molecular weight of 130 kg/mol is due to the transition to ordered state with increasing molecular weight. It is shown that block copolymers in the disordered state show a deterioration of tensile properties. Finally, ordered structures, intermediate segregation, and molecular weight of about 300 kg/mol are necessary for an optimization of mechanical properties of weakly segregated block copolymers.

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